

ANALYSIS OF CDTE ACTIVATION TREATMENT WITH A NOVEL APPROACH

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ABSTRACT: In this paper we propose a new approach for CdTe activation treatment. Starting from a baseline of CdTe devices made with CdCl₂ activation process we present a double treatment where CdCl₂ and Freon[®], namely difluorochloromethane, treatments are applied in sequence. This new activation process delivered solar cells with efficiencies well above 15%. The mechanisms for these improved efficiencies are studied by morphological (high resolution microscopy), structural (X-ray diffraction analysis) and electrical measurements (capacitance-voltage and current-voltage characteristics) of finished devices.

Keywords: CdTe, CdCl₂, High-Efficiency.

1 INTRODUCTION

CdTe thin film solar cells are the most successful thin film photovoltaic devices in terms of production yield, as attested by the latest market performance. Nevertheless this device has also shown to be competitive in terms of efficiency with the latest results from General Electric, where a record efficiency of 19.6% has been obtained [1].

Contrarily to other thin film devices, like CuInGaSe₂ and Cu₂ZnSnS₄, CdTe needs in order to perform high conversion efficiencies a morphological and electrical transformation which is generally given by an annealing of the CdTe layer after deposition of CdCl₂ at 400-430 °C in air [2].

Other successful activation treatments have also been applied such as annealing of the CdTe layer in argon and chlorine containing gases (such as Freon[®], namely difluorochloromethane) atmosphere at high temperature [3]. In former publications we have analyzed these different activation treatments on low temperature deposited CdTe device, by tuning the amount of CdCl₂ [4] and by changing the quantity of Freon[®] and temperature [5].

In this paper we compare our standard CdCl₂ treated CdTe with our Freon[®] treated CdTe and with absorbers that have been treated with both processes (double treatment). This so-called double treatment consists of annealing the CdTe at 400 °C in Freon[®] and Argon atmosphere followed by the CdCl₂ deposition in methanol solution and annealing in air. Solar cells with high efficiencies (above 15%) have been obtained with this process.

In this paper we present a thorough study of these differently treated devices that are compared with typical CdCl₂ treated devices in order to address the different effects of the new activation treatment.

2 EXPERIMENTAL

In our laboratory CdTe devices on superstrate configuration are prepared at temperatures not exceeding 450 °C.

As a substrate, a direct current sputtered indium tin oxide (ITO) plus radio frequency sputtered zinc oxide

(ZnO) coated glass is used. In the same vacuum chamber 300 nm of CdS and 6 microns of CdTe are deposited at substrate temperatures respectively of 100°C and 340°C.

As previously mentioned, the CdTe activation treatment is typically made by depositing a saturated solution of CdCl₂ in methanol and by annealing the stacks in a furnace at 410 °C.

Prior to the deposition of the back contact, the CdTe surface is etched by a bromine/methanol (Br-MeOH) solution in order to remove CdCl₂ residues and to make a p⁺ intermediate layer. The back contact is made by a subsequent evaporation of 2nm copper and 50nm gold in the same vacuum chamber at room temperature.

Structural analysis of CdTe layers by means of X-Ray diffraction (XRD), Atomic Force Microscopy (AFM) and electronic study of finished devices by means of current density-voltage (JV), capacitance-voltage (CV) and drive level capacitance profiling (DLCP) techniques are applied to clarify the effects of double chlorine treatment on the CdTe layers.

AFM was applied with a NT-MDT Solver Pro in semi-contact mode, XRD on the different absorber layers has been performed by a Thermo ARL X'TRA powder diffractometer, operating in Bragg-Brentano geometry equipped with a Cu-anode X-ray source (K α , λ =1.5418 Å) and using a Peltier Si(Li) cooled solid state detector.

JV characteristics are performed with a Keithley SourceMeter 2420 at room temperature with an irradiation of 1000W/m²; DLCP and CV study is made with a HP4284A LCR and with a Janis cryostat with Lakeshore 325 temperature controller in a vacuum of 10⁻⁶ mbar and in a range of temperature between 100 K and 320 K.

3 DISCUSSION

3.1 Introduction

In a previous work a thorough study of the effects of different quantity of CdCl₂-methanol solution with same annealing temperature has been presented [5]. From these studies efficiencies exceeding 14% are routinely obtained [6].

On the other hand a different treatment with chlorine containing gases, such as Freon[®], mixed with Argon has

been previously applied on our devices. Contrarily to close space sublimated solar cells [3], our vacuum evaporated CdTe devices have shown low efficiency not exceeding 9% [5]. In particular CV measurements have shown that electrical transformation of the absorbers was scarce, with low carrier concentration [7]. However the CV and DLCP characteristics of the devices with Freon[®] treated CdTe have also shown a very similar behavior with no difference on the amount of defects concentration proving a remarkably low presence of deep defects (see Fig.1).

For this reason difluorochloromethane annealing has been investigated further by combining the two different activation treatments together as mentioned above.

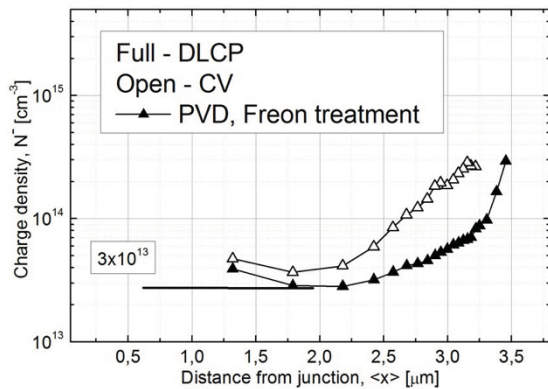


Figure 1: CV (open dots) and DLCP (full dots) measurements of a Freon[®] treated device

3.2 Structural analysis

The back contact and the rest of the layers composing the cell have been prepared with the same parameters in order to address the different properties.

As shown in Fig. 2, double treated CdTe layers have a different morphology with a grain size similar to that of the CdCl₂ treated layer, however larger than the Freon[®] treated CdTe ones. This is suggesting that despite a strong recrystallization has already occurred, after CdCl₂ activation however the layer can be still transformed by the Freon[®] treatment, changing the structural properties.

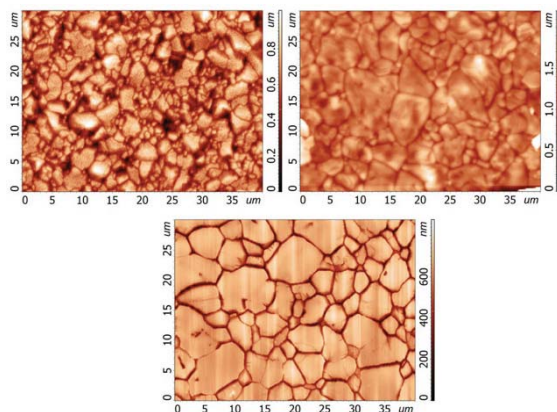


Figure 2: AFM pictures of Freon, CdCl₂ and double treated CdTe layers (clockwise)

XRD patterns have been measured and analyzed in order to study the CdTe recrystallization also by a crystallographic point of view.

Generally our CdTe layers grow strongly (111) oriented, becoming then randomized after CdCl₂

treatment, however the Freon treated sample do not change their preferential orientation very much [5]. Double treated CdTe layers show a loss in preferential orientation but with a less randomized structure (not shown here). Most interesting is to take into account the Nelson-Taylor plot, which is a method to calculate the lattice parameter with very high accuracy from the XRD patterns [8,9].

The calculation states, as shown in Fig.3, that not a significant change of the lattice parameter is registered. This suggests that there is no influence in the intermixing of the CdS/CdTe layers and no particular difference in the formation of CdS_xTe_{1-x} solid solution from the application of double treatment compared to standard CdCl₂ treated stacks.

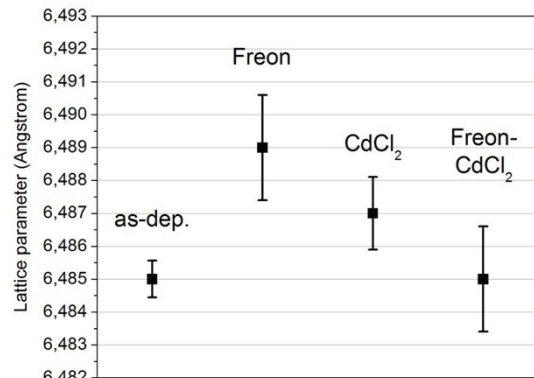


Figure 3: Results of lattice parameter calculation by Nelson-Taylor plot; CdCl₂ and double treated CdCl₂+Freon layers show a similar lattice path

3.3 Electrical analysis

A subsequent double activation treatment could be seen just as a stronger annealing, with no real influence of the gas activation treatment, for this reason we have compared double treated CdTe photovoltaic devices with devices made by over treating the CdTe layers also presented in one of our previous work [4]. This last samples were made by depositing 10 times the amount of CdCl₂ solution than the standard treatment. In figure 3, (DLCP and CV graphs of over-treated, double treated and standard treated (in the inset, bottom picture) CdTe layers are shown. The most interesting fact is that the devices are actually very different in terms of electronic properties demonstrating that we cannot consider the double treatment process just as over-treating the CdTe layers.

In particular what is remarkable is that for the double treated case there is a very small difference between DLCP and CV away from the junction, demonstrating a very low concentration of deep defects, compared to the standard CdCl₂ treatment. Even at different frequency the CV and DLCP curves stay very near, showing that there is no switch-off effects of the deep traps, but that actually for this sample the deep traps are almost silenced (see Fig. 4).

As mentioned above this phenomenon cannot be attributed just to an excess amount of CdCl₂, as shown by the CV and DLCP measurements of over treated samples. In this case, indeed, the difference is actually very evident, and on the contrary it seems that with an excess of CdCl₂ a larger amount of deep traps is observed.

Moreover if we compare Fig.1 with the second picture of Fig.4 we can observe that effect of deep level

minimization is repeated but with double treatment the shallow defects concentration (DLCP) is one order of magnitude higher than the one activated only by difluorochloromethane.

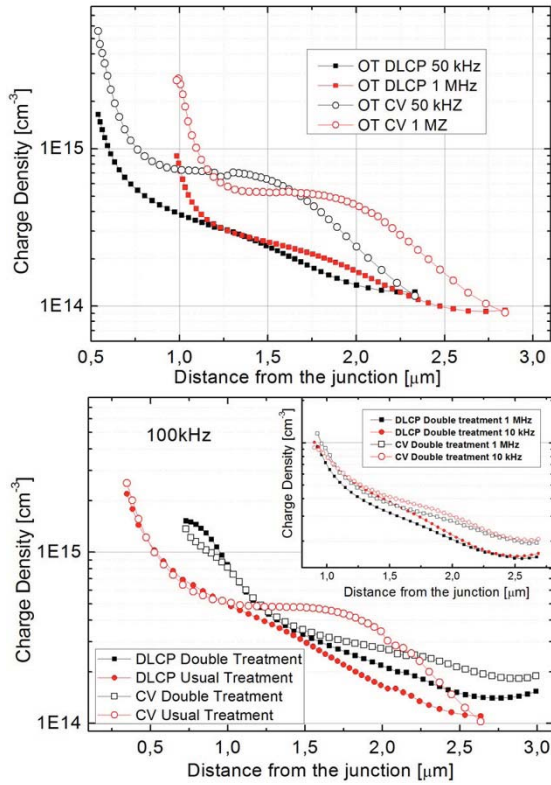


Figure 4: CV and DLCP measurements of devices with over treated (top), CdCl₂ treated and double treated (bottom) CdTe solar cells at different frequencies

These results are actually confirmed by the current-voltage measurements of the double treated devices (see Fig. 5), where a remarkable efficiency, higher than the standard CdTe activation treatment is registered. In particular very similar values of open circuit voltage and fill factor are observed, but a very strong difference for current density is observed which is in accordance with what is observed by the CV and DLCP measurement.

Efficiencies exceeding 15% are obtained with double treatment and a low temperature deposition process.

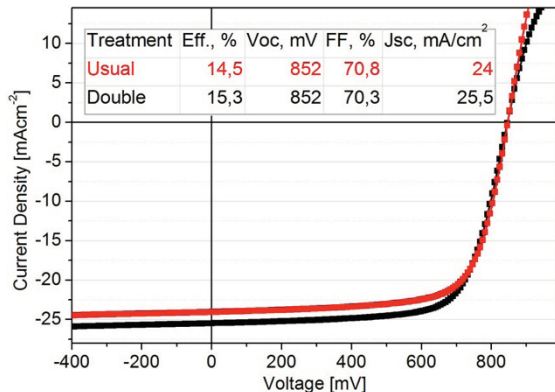


Figure 5: IV measurements of devices made with CdTe treated by CdCl₂ and by double treatment

4 CONCLUSIONS

A new activation treatment by subsequent CdCl₂ and Freon annealing processes has been introduced.

This new process performs a larger CdTe grains size but without changing the structural properties given by the initial CdCl₂ treatment and by keeping the same balance of CdS_xTe_{1-x} solid solution.

Most important, a low level of deep defects is reproduced as was in the Freon treatment case but with much higher carrier concentration delivering efficiencies above 15%.

A better optimization of the process with enhanced carrier density could give top efficiencies also with the low temperature process, which has lower energy consumption.

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